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## REMARKS

Entry of the foregoing amendments, and reexamination and reconsideration of the subject application, pursuant to and consistent with 37 C.F.R. § 1.104 and § 1.112, and in light of the following remarks, are respectfully requested.

### Rejections under §103

Prior to addressing the rejections hereunder, Applicants would first remark that the primary reference in all of the rejections, WO '792, does not disclose a thin film and does not disclose an M-X-Y granular material.

As shown in the two attached excerpts (from *The Encyclopedia of Physics* (New York: Van Nostrand Reinhold Co., 1974) and *Dictionary of Scientific and Technical Terms*, 5<sup>th</sup> Ed. (New York: McGraw-Hill, Inc., 1994)), the term "thin film", especially as applied in the electronic arts relating to the present invention, means a film generally a few molecules (*Dict.*) or a few microns (*Ency.*) thick. The *Encyclopedia* mentions that thin films are typically made by vapor deposition, sputtering, or the like (see present application at page 6, line 7).

More importantly, WO '792 discloses that iron, iron oxide, nickel, cobalt, etc. as disclosed is dispersed in a resin: "resins for adhesion, such as a polyester system, are made to *distribute* a magnetic material (\*\*\*\*\* shield material)." (At the cited ¶ [0016] in WO '792; italics added.) The structure and material of the reference is a dispersion of a "shield material" in a resin, and not the claimed "granular form" thin film material claimed.

Further regarding a "granular" material, attached is an article (Chien, "Granular magnetic solids," *J. Appl. Phys.* 69 (8), 15 April 1991) explaining

fabrication and various characteristics of granular materials. None of the materials disclosed therein includes a dispersion of particles in a resin matrix: granular materials "consist of small metal granules embedded in an immiscible medium which may be insulating" and such insulators include silica, alumina, and magnesia (top and bottom of col. 1 of Chien).

Therefore, WO '792 does not disclose a thin film as that term is used in the present application, and does not disclose a granular M-X-Y material.

Iwasaki *et al.* do disclose a thin film, but they disclose a thin film having a "crystal structure at least partially consisting of an fcc phase" (abstract). The fcc crystalline phase is important for Iwasaki *et al.*'s invention (col. 1, ln. 35-40). Nowhere in this reference are magnetic losses mentioned. Rather, this reference is concerned not with shielding (in which magnetic losses are desired) but with making a good quality recording head (in which magnetic losses are not desirable).

Livshits *et al.*, identical with WO '792, discloses that magnetic particles can be dispersed in "a dielectric matrix of an organic resin" (col. 3, ln. 12-13); see also col. 6, first paragraph, wherein a "paste" of a mixture of the magnetic particles and a "binder" is "moulded and/or otherwise processed like conventional plastic or ceramic materials for IC packaging" and "cured."

Yoshida *et al.*, again like WO '792, disclose metallic powders dispersed in a resin. That the particles can be made by "grinding, rolling," or the like means only that the magnetic particles are granules, *whereas* the present claims recite a thin film having a granular form. In this reference, the granules are only the magnetic particles, which is not a granular material. Based on the attached

Chien article it is clear that a “granular” thin film refers to “nanometer size metal particles” (abstract) dispersed in a thin film.

A) Claims 1-4 stand rejected as obvious over WO '792 in view of Iwasaki (*et al.*) and Livshits (*et al.*), which rejection is respectfully traversed. As explained above, WO '792 and Livshits describe dispersions of particles in a resin binder. Neither discloses a thin film of a granular M-X-Y composition wherein M is dispersed in an X-Y matrix; rather, the references disperse the particles in a resin matrix. Iwasaki does disclose a thin film but one that has a crystalline structure, not one having a granular structure.

Without any literal description of a “thin film” or any mention of the processes (vapor deposition, sputtering) conventionally used to make thin films, there is no objective support for the proposition in the rejection that WO '792 teaches a thin film. Accordingly, the combination of WO '792 and Iwasaki is improper, because the former disperses particles in a binder matrix while the latter discloses a crystalline thin film without any dispersion of particles. At best, the materials used by Iwasaki to make a thin film, or disclosed by Livshits as dispersed in an organic (resin) matrix, might be used in the resin dispersion of WO '792, but that resin matrix does not render obvious claims 1-4.

B) Claims 1-9, 11-14, and 16-18 stand rejected as obvious over WO '792 in combination with Yoshida (*et al.*) and Livshits (*et al.*), which rejection is respectfully traversed.

Contrary to the allegation in the rejection, Yoshida does not disclose dispersal of metal particles in an insulating alumina or silica matrix, but rather

that the particles are "provided with a dielectric outer surface layer so as to electrically isolate each power particle from adjacent powder particles" where the dielectric layer is formed by oxidizing the outer surface of each particle (col. 4, ln. 59-67; underline added). That is, even in "high powder loaded density," that is, when a resin is highly loaded with these oxidized particles, the particles are electrically isolated from each other. A highly loaded resin is not a thin film.

Because these references each teach various powders dispersed in a resin binder, it may have been obvious to use the Yoshida or Livshits powder in WO '792, but that combination still does not render obvious the claimed granular thin film magnetic material.

C) Claim 15 stands rejected as obvious over WO '792 in view of Iwasaki, Yoshida, and Livshits, which rejection is respectfully traversed. As noted above, only Iwasaki is directed to thin films, although crystalline thin film as opposed to granular thin films as claimed. There is no basis shown in the rejection how to substitute the thin film of Iwasaki for the powder-resin combination of the other three references, to say nothing of making such a thin film in a granular form of the composition as claimed.

### Conclusion

It appears that the primary issues, or misunderstandings, in the rejection relate to (a) thin films and (b) granular materials. It is Applicants' contention that, in these arts, a thin film is a film having a thickness on the order of micrometers (or smaller), and in no way would be understood by the artisan of ordinary skill to include a dispersion of particles in a dielectric resin binder on the order of

millimeters thick. Further, the magnetic properties of the claimed thin film are due to the entire composition of the film, whereas in the art resin-powder film, the magnetic shielding properties are due solely to the powder. It is also Applicants' contention that the "granular" aspect of the thin film, as would be understood by one of ordinary skill in these arts, does not relate to the use of a powder (that is, granules), but rather would be understood to mean that the unitary thin film composition has a granular structure at the smallest level (Chien).

Accordingly, withdrawal of all of the rejections is believed to be in order. If the rejections are to maintained, it is suggested first that a telephonic interview be held among the Examiner, his supervisor, and the undersigned to resolve these two issues that appear to be the primary obstacles in this prosecution.


Respectfully submitted,

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3 June 2004

# THE ENCYCLOPEDIA OF PHYSICS

SECOND EDITION

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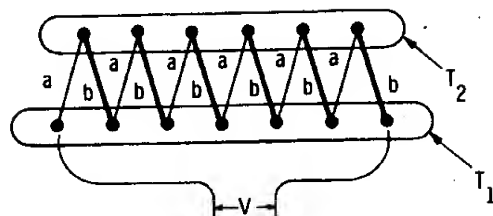


FIG. 2. A thermopile made from materials a and b. All of the upper junctions are at temperature  $T_2$  and all of the lower ones are at temperature  $T_1$ .

Devices have also been built utilizing the Seebeck effect to generate electricity directly from a heat source and utilizing the Peltier effect for refrigeration or heat pumping. In these applications the thermoelectric materials are semiconductors, such as  $\text{Bi}_2\text{Te}_3$ ,  $\text{PbTe}$  or  $\text{GeTe}$ , with a diameter of 0.3 to 1.3 cm and a length of 0.3 to 2 cm. The introduction of a magnetic field into a material may change its Seebeck, Peltier, and Thomson coefficients; it also produces several new effects, called galvanomagnetic and thermomagnetic effects. These include the Nernst, Ettingshausen, and Righi-Leduc effects. In these effects, the electric current or electrical potential difference, the magnetic field, and the temperature gradient or heat flow are all mutually perpendicular. These effects have also been used as a basis for devices which will pump heat or generate electricity directly from a temperature gradient (see HALL EFFECT AND RELATED PHENOMENA).

ROLAND W. URE, JR.

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Cross-references: CONDUCTIVITY, ELECTRICAL; HALL EFFECT AND RELATED PHENOMENA; TEMPERATURE AND THERMOMETRY.

#### THIN FILMS

General The term "thin films" is used for a wide variety of physical structures. Self-supporting solid sheets usually are called foils when thinned from thicker material by such methods as rolling, beating, or etching; and films, when obtained by stripping a deposited layer from its substrate. Supported thin films are deposited on planar or (in special cases) curved substrates by such methods as vacuum evaporation, cathode sputtering, electroplating, electroless plating, spraying, and various chemical surface reactions in a controlled atmosphere or electrolyte. Thicknesses of such supported films range from less than an atomic monolayer to a few microns ( $1\mu = 10^{-4}$  cm). A frequently used thickness measure is the angstrom ( $1\text{\AA} = 10^{-8}$  cm). Thin films not forming a continuous sheet are called "island films." Particularly, noble metals may condense as islands of considerable thickness (up to  $\sim 10^2 \text{\AA}$ ).

In scientific studies and technical applications, the use of well-controllable deposition methods such as vacuum evaporation and cathode sputtering are generally preferred. The film structure is markedly influenced by such deposition parameters as substrate composition and surface structure, source and substrate temperatures, deposition rate, and composition and pressure of the ambient atmosphere (where applicable). In general, the structure of films is more disordered than the corresponding bulk material. Smaller grains, higher dislocation concentrations, and deviations from stoichiometry are typical, and films approach bulk structure only as a limiting case. Under certain growth conditions, films exhibit preferential crystal orientations or even epitaxy. (Epitaxy means that the film structure is determined by the crystal structure and orientation of the underlying substrate.)

Solid thin films are common study objects in most phases of solid-state physics. They supply the samples for the study of general structural and physical properties of solid matter where special beam methods require small quantities of material or extremely thin layers, as for instance in transmission electron microscopy and diffraction, NEUTRON DIFFRACTION, UV spectroscopy, and X-RAY DIFFRACTION and SPECTROSCOPY. Thin films represent the best means for studying physical effects, where these effects are caused by the extreme thinness of the material itself. Examples are the rotational switching of ferromagnetic films, electron tunneling phenomena, electromagnetic skin effects of various kinds, and certain optical interference phenomena (see FERROMAGNETISM, SKIN EFFECT and TUNNELING). Films also are convenient vehicles for the investigation of nucleation and crystal growth, and for states of extremely disturbed thermodynamic equilibrium.

Presently, films find three major industrial uses: the decorative finishing of plastics, optical coatings of various kinds (mainly antireflection

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coatings, reflection increasing films, multilayer interference filters, and fluorescent coatings), and in electronic components from transistors or resistor-capacitor networks to such specialized devices as magnetic storage bits, photosensors, and cryotrons. The restricted space only permits the discussion of a few selected research and application areas.

**Nucleation, Growth and Mechanical Properties of Films** In vacuum evaporation, molecules or atoms of thermal energy are deposited at a uniform angle of incidence and under well-defined environmental conditions. Most nucleation and growth studies, therefore, have been made on evaporated films. A particle approaching the substrate enters close to its surface a field of attracting short-range London forces with an exchange energy proportional to  $-1/r^6$ . At a still shorter distance  $r$ , repulsive forces proportional to  $e^{-r/\text{constant}}$  resist the penetration of the electron clouds of the surface atoms. Due to the atomic or crystalline structure of the substrate, this potential field exhibits periodicity or quasiperiodicity in the substrate plane. The freshly condensed particles migrate over the surface with a jump frequency  $i_D \propto \exp(-Q_D/kT)$ , or desorb with a frequency  $i_{ad} \propto \exp(-Q_{ad}/kT)$ , where the activation energy  $Q_D$  is often approximately one-fourth of  $Q_{ad}$ . Permanent condensation occurs in most cases at distinct nucleation centers which may consist of deep potential wells of the substrate, clusters of condensed particles, or previously deposited "seed" particles of a different material. The number of nuclei formed in the second case is strongly temperature and rate dependent.

Most metals always condense in crystalline form, but the grain size is extremely small at low temperatures (on the order of a few angstroms) and increases markedly with increasing substrate temperatures. Grain size decreases with increasing deposition rates. The condensation of amorphous or quasi-liquid phases at low temperatures has been observed for such metals as antimony and bismuth and a few dielectrics. Some of these materials, on annealing, pass through otherwise unobserved, and probably metastable, phases.

Stresses of considerable magnitude are often observed in deposited films. The main causes of these stresses are a mismatch of expansion coefficients between substrate and film, enclosed impurity atoms, a high concentration of lattice defects and, in very thin films, a variety of surface effects. Often, the stresses resulting from lattice defects can be minimized by the choice of a higher substrate temperature during deposition, or they can be reduced by a post-deposition anneal. Metal films frequently exhibit tensile strengths which are considerably larger than those of the corresponding bulk materials.

**Thin-film Optics** Deposited metal mirrors probably represent the oldest optical application of films. High-quality mirrors usually are pro-

duced by the vacuum evaporation of aluminium on an appropriately shaped glass substrate. Often, a glow-discharge cleaning of the substrate or a chromium undercoat is first applied to increase the adhesion of the aluminium. After deposition, the aluminium is protected by anodic oxidation or an evaporated overcoat of  $\text{SiO}_2$ ,  $\text{SiO}_2$ , or  $\text{Al}_2\text{O}_3$ .

For  $\text{SiO}_2$ , maximum reflectance in the visible spectral region is achieved at a thickness of about  $1400\text{\AA}$ . Rapid  $\text{SiO}_2$  evaporation reduces the reflectance at shorter wavelengths.

Single or multilayer coatings find increasing use as optical interference filters. These film stacks may consist solely of transparent films of different refractive indices  $n_f$ , or a combination of absorbing and nonabsorbing layers. Common low-index materials for glass coatings in the visible region of the spectrum are  $\text{MgF}_2$  ( $n_f = 1.32$  to  $1.37$ ), and cryolite  $\text{Na}_3\text{AlF}_6$  ( $n_f = 1.28$  to  $1.34$ ); high-index materials are  $\text{SiO}_2$  ( $n_f = 1.97$ ),  $\text{ZnS}$  ( $n_f \approx 2.34$ ),  $\text{TiO}_2$  ( $n_f = 2.66$  to  $2.69$ ) and  $\text{CeO}_2$  ( $n_f = 2.2$  to  $2.4$ ). The indices are given for the sodium D line. Various semiconductors are used for infrared coatings.

At each air-film, film-film, or film-substrate interface, the incident light amplitude is split into a reflected and a transmitted fraction according to the Fresnel coefficients

$$f_{j-1} = (\hat{n}_{j-1} - \hat{n}_j) / (\hat{n}_{j-1} + \hat{n}_j) \text{ and} \\ g_{j-1} = 2\hat{n}_{j-1} / (\hat{n}_{j-1} + \hat{n}_j)$$

where  $j$  and  $j-1$  denote the number of the optical layer counted from the side of the incident beam.  $\hat{n}_j = n_j / \cos \Theta_j$  for  $p$  polarization or  $\hat{n}_j = n_j \cos \Theta_j$  for  $s$  polarization is the effective refractive index, and  $n_j = n_j - ik_j$  the refractive index of the  $j$  layer.

$$\cos \Theta_j = \sqrt{(\sqrt{p_j^2 + q_j^2} + p_j) / 2} \\ - i \sqrt{(\sqrt{p_j^2 + q_j^2} - p_j) / 2}$$

$$p_j = 1 + (k_j^2 - n_j^2) [n_0 \sin \theta_0 / (n_j^2 + k_j^2)]^2 \\ q_j = 2n_j k_j [n_0 \sin \theta_0 / (n_j^2 + k_j^2)]^2$$

The symbol  $\theta_0$  is the angle of incidence in the incident medium.

For nonabsorbing film stacks ( $k_i = 0$ ;  $i = 1, 2, \dots, m+1$ ), the over-all reflectance and transmittance may be obtained by summing the multiple coherent reflections between the film boundaries. A more general treatment based on electromagnetic theory yields for amplitude reflectance and transmittance the recursion formulas

$$r_{(j-1)} = (f_{j-1} + r_j \exp(-2i\hat{\Phi}_j)) / \\ (1 + f_{j-1}r_j \exp(-2i\hat{\Phi}_j))$$

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On the cover: Photomicrograph of crystals of vitamin B<sub>1</sub>.  
(Dennis Kunkel, University of Hawaii)

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zation with those immediately surrounding it; the bisectors form a series of polygons, each polygon containing one station; the value of precipitation measured at a station is assigned to the whole area covered by the enclosing polygon. ( 'tē-sən 'pāl-igən ,meth-əd )

**high** [ANAT] The upper part of the leg, from the pelvis to the knee. ( 'thī )

**high circumference** [ANTHRO] The measurement around the thigh of the left leg midway between the crotch and the knee when the subject is in a standing position. ( 'thī sər,kəm-frəns )

**thigmotaxis** See stereotaxis. ( 'thig-mə'tak-səs )

**thigmotrichida** [INV ZOO] An order of ciliated protozoans in the subclass Holotrichia. ( 'thig-mō'trik-əd-ə )

**thigmotropism** See stereotropism. ( 'thig'mā-trə,piz-əm )

**thill** See underclay. ( 'thīl )

**thimble** [COMPUT SCI] A cone-shaped, rotating printing element on an impact printer having character slugs around the perimeter and a hammer that drives the appropriate slug forward to print the impression on paper. ( 'thim-bəl )

**thimble ionization chamber** [NUCLEO] A small cylindrical or spherical ionization chamber, usually with walls made of organic material or air walls. ( 'thim-bəl ,i-ə-nə'zā-shən ,chām-bar )

**thin** [METEOROL] In aviation weather observations, the description of a sky cover that is predominantly transparent. ( 'thin )

**thin-bedded** [GEOL] Pertaining to a sedimentary bed that ranges in thickness from 2 inches to 2 feet (5 to 60 centimeters). ( 'thin ,bed-əd )

**thin film** [ELECTR] A film a few molecules thick deposited on a glass, ceramic, or semiconductor substrate to form a capacitor, resistor, coil, cryotron, or other circuit component. [MATER] A film of a material from one to several hundred molecules thick deposited on a solid substrate such as glass or ceramic or as a layer on a supporting liquid. ( 'thin 'film )

**thin-film capacitor** [ELEC] A capacitor that can be constructed by evaporation of conductor and dielectric films in sequence on a substrate; silicon monoxide is generally used as the dielectric. ( 'thin 'film kə'pas-əd-ər )

**thin-film circuit** [ELECTR] A circuit in which the passive components and conductors are produced as films on a substrate by evaporation or sputtering; active components may be similarly produced or mounted separately. ( 'thin 'film 'sər-kət )

**thin-film cryotron** [ELECTR] A cryotron in which the transition from superconducting to normal resistivity of a thin film of tin or indium, serving as a gate, is controlled by current in a film of lead that crosses and is insulated from the gate. ( 'thin 'film 'krī-ə, trən )

**thin-film ferrite coil** [ELECTROMAG] An inductor made by depositing a thin flat spiral of gold or other conducting metal on a ferrite substrate. ( 'thin 'film 'fe,rīt 'kōil )

**thin-film field-emitter cathode** [ELECTR] A sharply pointed microminiature electron field emitter with an integral low-voltage extraction gate. ( 'thin 'film 'fēld i,mīd-ər 'kath,əd )

**thin-film integrated circuit** [ELECTR] An integrated circuit consisting entirely of thin films deposited in a patterned relationship on a substrate. ( 'thin 'film 'int-ə,grād-əd 'sər-kət )

**thin-film material** [ELECTR] A material that can be deposited as a thin film in a desired pattern by a variety of chemical, mechanical, or high-vacuum evaporation techniques. ( 'thin 'film mō'tir-ē-əl )

**thin-film memory** See thin-film storage. ( 'thin 'film 'mem-rē )

**thin-film resistor** [ELEC] A fixed resistor whose resistance element is a metal, alloy, carbon, or other film having a thickness of about 0.000001 inch (25 nanometers). ( 'thin 'film rī'zīst-ər )

**thin-film semiconductor** [ELECTR] Semiconductor produced by the deposition of an appropriate single-crystal layer on a suitable insulator. ( 'thin 'film 'sem-i-kən,dəkt-ər )

**thin-film solar cell** [ELECTR] A solar cell in which a thin film of gallium arsenide, cadmium sulfide, or other semiconductor material is evaporated on a thin, flexible metal or plastic substrate; the rather low efficiency (about 2%) is compensated by the flexibility and light weight, making these cells attractive as power sources for spacecraft. ( 'thin 'film 'sō-lər 'sel )

**thin-film storage** [COMPUT SCI] A high-speed storage device that is fabricated by depositing layers, one molecule thick, of various materials which, after etching, provide microscopic cir-

cuits which can move and store data in small amounts of time. Also known as thin-film memory. ( 'thin 'film 'stōr-ij )

**thin-film transducer** [SOLID STATE] A film a few molecules thick, usually consisting of cadmium sulfide, evaporated on a crystal substrate, used to convert microwave radiation into hypersonic sound waves in the crystal. ( 'thin 'film tranz'dü-sər )

**thin-film transistor** [ELECTR] A field-effect transistor constructed entirely by thin-film techniques, for use in thin-film circuits. ( 'thin 'film tran'zīst-ər )

**think time** [COMPUT SCI] Idle time between time intervals in which transmission takes place in a real-time system. ( 'thɪŋk ,tīm )

**thin-layer chromatography** [ANALY CHEM] Chromatographing on thin layers of adsorbents rather than in columns; adsorbent can be alumina, silica gel, silicates, charcoals, or cellulose. ( 'thin ,lā-ər ,krō-mə'täg-rə-fē )

**thin lens** [OPTICS] A lens whose thickness is small enough to be neglected in calculations of such quantities as object distance, image distance, and magnification. ( 'thin 'lenz )

**thin list** See loose list. ( 'thin 'list )

**thinner** [MATER] A liquid used to thin paint, varnish, cement, or other material to a desired consistency. ( 'thin-ər )

**Thincoridae** [VERT ZOO] The seed snipes, family of South American birds in the order Charadriiformes. ( ,thin-ə'kōr-ə,dē )

**thin-out** [GEOL] Gradual thinning of a stratum, vein, or other body of rock until the upper and lower surfaces meet and the rock disappears. ( 'thin'au̯t )

**thin-plate orifice** [ENG] A thin-metal orifice sheet used in fluid-flow measurement in fluid conduits by means of differential pressure drop across the orifice. ( 'thin 'plāt 'ōr-ə-fās )

**thin section** [GEOL] A piece of rock or mineral specifically prepared to study its optical properties; the sample is ground to 0.03-millimeter thickness, then polished and placed between two microscope slides. Also known as section. ( 'thin 'sek-shən )

**thin-skinned structure** [GEOL] Any large-scale structure, such as a fold or fault, confined to and originating within a thin layer of rocks above a surface of décollement. ( 'thin 'skɪnd 'strʌk-ʃər )

**thio-** [CHEM] A chemical prefix derived from the Greek *theion*, meaning sulfur; indicates the replacement of an oxygen in an acid radical by sulfur with a negative valence of 2. ( 'thī-ō )

**thioacetamide** [ORG CHEM] C<sub>2</sub>H<sub>5</sub>NS A crystalline compound with a melting point of 113–114°C; soluble in water and ethanol; used in laboratories in place of hydrogen sulfide. ( 'thī-ō-ə'sed-ə'mīd )

**thioacetic acid** [ORG CHEM] CH<sub>3</sub>COSH A toxic, clear-yellow liquid with an unpleasant aroma, soluble in water, alcohol, and ether, boils at 82°C; used as an analytical reagent and a lacrimator. Also known as thiocetic acid. ( 'thī-ō-ə'sed-ik 'as-əd )

**thioaldehyde** [ORG CHEM] An organic compound that contains the —CHS radical and has the suffix -thial; for example, ethanethial, CH<sub>3</sub>CHS. ( 'thī-ō'al-də,hīd )

**Thiobacteriaceae** [MICROBIO] Formerly a family of nonfilamentous, gram-negative bacteria of the suborder Pseudomonadineae characterized by the ability to oxidize hydrogen sulfide, free sulfur, and inorganic sulfur compounds to sulfuric acid. ( 'thī-ō-bak,tir-ē'ās-ē,ē )

**thiobarbiturate** [PHARM] A derivative of thiobarbituric acid that differs from the barbiturates in the replacement of one oxygen atom by sulfur but resembles the barbiturates in its effects. ( 'thī-ō-bār'bich-ə,rāt )

**thiobarbituric acid** [ORG CHEM] C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>O<sub>2</sub>S Malonyl thiourea, the parent compound of the thiobarbiturates; represents barbituric acid in which the oxygen atom of the urea component has been replaced by sulfur. ( 'thī-ō,bār-bə'tür-ik 'as-əd )

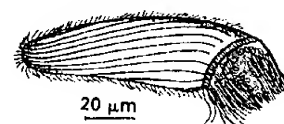
**thiocarbazine** [PHARM] C<sub>21</sub>H<sub>17</sub>AsN<sub>2</sub>O<sub>3</sub>S<sub>2</sub> A white crystalline powder, freely soluble in dilute alkali; used in medicine as an amebicide. ( 'thī-ō-kār'bām-ə,zēn )

**thiocarbamide** See thiourea. ( 'thī-ō'kār-bə,mīd )

**thiocarbaniide** [ORG CHEM] CS(NHC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> A gray powder with a melting point of 148°C; soluble in alcohol and ether; used for making dyes, and as a vulcanization accelerator and ore flotation agent. Also known as sulfoarbanilide. ( 'thī-ō,kār-bə'ni,līd )

**thiocarbarsone** [PHARM] C<sub>11</sub>H<sub>13</sub>AsN<sub>2</sub>O<sub>3</sub>S<sub>2</sub> A white crys-

# THIGMOTRICHIDA



Drawing of *Boveria*, an example of a thigmotrichid, showing ciliation.

# Granular magnetic solids (invited)

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Granular metals consist of nanometer size metal granules embedded in an immiscible medium. They display a rich variety of physical properties as a result of their unique nanostructure and extra degrees of freedom. They are also suitable for the exploration of finite-size effects, enhanced and tailored properties of fundamental interest, and for technological applications. Granular magnetic solids of elemental metals and alloys will be discussed. Single-domain characteristics, superparamagnetic relaxation, enhanced ferromagnetic properties, granular alloys, and spin glasses are some of the topics covered.

## I. INTRODUCTION

Granular solids<sup>1,2</sup> consist of small metal granules embedded in an immiscible medium which may be insulating or, less frequently, metallic.<sup>3</sup> Like other artificially structured solids, granular solids contain intricate structure on the nanometer scale and extra degrees of freedom with which the physical properties can be manipulated to achieve tailored materials for applications and for explorations of physical phenomena. The relevant extra degrees of freedom of granular solids are the granule size, which can be controlled by process conditions, and metal volume fraction ( $x_v$ ), which can be experimentally varied between 0 and 1. For the samples with small values of  $x_v$ , the metal granules are isolated from each other and protected by the insulating matrix. Electrically, granular solids with low  $x_v$  are insulating, apart from tunneling among metallic grains, which is of course interesting in its own right. In magnetic granular solids, all such granules are single domain exhibiting "hard" magnetic properties. On the other hand, for samples with large values of  $x_v$ , the metal granules form an infinite network, exhibiting metallic conductivity and "soft" magnetic properties, since the conducting paths and magnetic closure structure are readily facilitated. The percolation threshold ( $x_p$ ) is the volume fraction at which an infinite network of metal granules first forms. Experimentally, for a wide variety of granular metal solids, the value of  $x_p$  has been found to lie in the range of 0.5–0.6.<sup>1,2</sup> For most common metals (e.g., Fe, Au, Co, Cu), the ultrafine solid granules can be made as small as 10 to a few hundred Å. This size range is much smaller than that achievable by traditional metallurgical and chemical methods. This is also the size range where finite-size effects, single-domain magnetic properties, and other phenomena may be observed. Because of their unique nanostructures, granular solids display a particularly rich variety of interesting conducting, superconducting, optical, magnetic, mechanical and other physical properties.<sup>1,2</sup>

Many granular solids consist of a metal and an insulator, the latter includes  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , etc. Granular solids are therefore also nanocomposite materials, which can reap benefits from both components. Since these insulators are usually mechanically harder, and more wear and corrosion resistant than the metal companion, granular metals exhibit superior auxiliary properties in addition to their attractive physical properties.

In this paper, we will primarily discuss the magnetic properties of a variety of granular magnetic solids. We will present extensive results of single element (e.g., Fe, Ni) granules in an insulating matrix. Some recent results of granular alloys, and results of granular metals embedded in a metallic medium, will also be discussed. Finally, in addition to our results on ferromagnetic magnetic granules, some recent studies of spin-glass granules will also be mentioned.

## II. FABRICATIONS AND CHARACTERIZATIONS

Granular solids can be made by a variety of deposition methods, of those, sputtering has been demonstrated to be the most versatile. Sputtering is most often administered using a single homogenous target, or cosputtering. Sequential deposition<sup>4</sup> is also applicable in some cases, if layer formation can be avoided. Since the nanostructures of granular metal solids are strongly influenced by the process conditions, deposition parameters such as deposition rate, sputtering pressure, and substrate temperature must be tightly controlled. The total film thicknesses are usually in the range of a few  $\mu\text{m}$ 's.

Because the density of the metal granules is generally different from that of the matrix they are embedded in, the metal volume fraction can be quite different from the atomic composition. For example,  $\text{Fe}_{50}(\text{SiO}_2)_{50}$  in atomic percent is equivalent to  $\text{Fe}_{21}(\text{SiO}_2)_{79}$  in volume percent. The all important metal volume fraction must of course be established using electron microprobe, Auger spectroscopy, energy-dispersive x-ray analysis, or wet chemistry.

Since the intricate structure of granular solids exists only on the nanometer scale, the use of transmission electron microscopy (TEM) is imperative. An example of TEM micrographs is shown in Fig. 1. The granules are equiaxial in shape, having sizes in the nanometer range with a rather narrow size distribution. For specimens with high volume fractions, the metallic grains form a connecting network, enclosing isolated regions of the second, usually insulating, medium.

X-ray and electron diffraction are additional techniques used to establish the structure of the ultrafine metal particles. Despite the broad peaks, the x-ray diffraction data unequivocally show the crystal structure and lattice parameter of the granules, in spite of their small sizes. In the cases of magnetic granular solids, the magnetic prop-



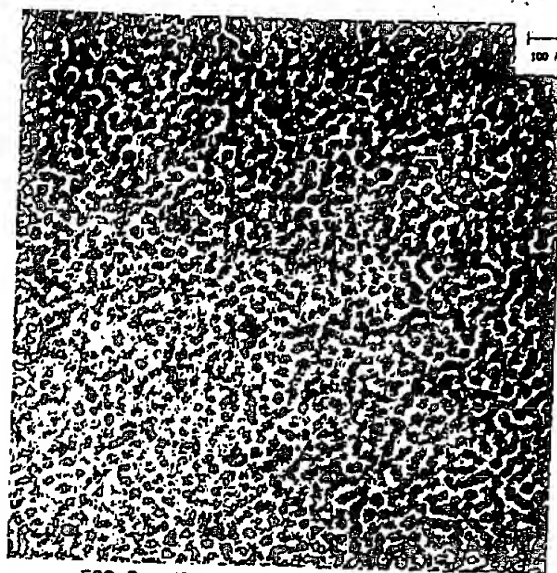


FIG. 1. Bright-field TEM micrograph of granular  $\text{Fe}_{70}(\text{SiO}_2)_{30}$  with 42 vol. % of Fe deposited at room temperature.

erties provide additional information about the granule sizes and their distribution.

### III. SINGLE-DOMAIN PARTICLES AND SUPERPARAMAGNETISM

For ultrafine magnetically ordered particles, there exists a critical size below which the granules can acquire only single magnetic domains even in zero magnetic field.<sup>5,6</sup> The critical sizes for Fe, Ni, and Co are of the order of a few hundreds of Å depending on the shape of the particle. The magnetic axis of a single-domain particle is determined by the magnetic anisotropy energy ( $CV$ ) of the particle, where  $C$  is total magnetic anisotropy energy per unit volume and  $V$  is the volume of the particle. At low temperatures, the magnetic axes of the single-domain particles are randomly oriented and frozen. This leads to a zero magnetization of the sample. Under a large external field, all the magnetic axes will be aligned, giving rise to the saturation magnetization ( $M_s$ ). When the external field is turned off, one measures the remanent magnetization ( $M_r$ ) which generally obeys  $M_r = \frac{1}{2}M_s$ , because the magnetic axes are randomly oriented over a hemisphere and  $\langle \cos \theta \rangle = \frac{1}{2}$ . These features are shown in Fig. 2. In fact  $M_r = \frac{1}{2}M_s$  at  $T = 0$  K is an experimental signature expected for all samples with well-separated ultrafine particles and randomly distributed magnetic easy axes.<sup>6</sup>

At sufficiently high temperatures, the magnetic anisotropy energy barriers of the single-domain particles are overcome by thermal energy, and superparamagnetism occurs. In the simplest analysis, superparamagnetic relaxation in zero applied field can be described by the Arrhenius law<sup>4</sup>

$$\tau = \tau_0 e^{CV/k_B T}, \quad (1)$$

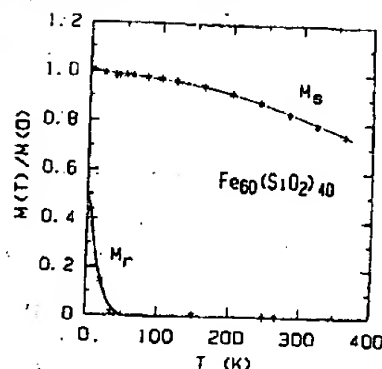


FIG. 2. Normalized magnetization ( $M_s$ ) at 50 kOe and remanent magnetization ( $M_r$ ) of  $\text{Fe}_{60}(\text{SiO}_2)_{40}$  as a function of temperature.

where  $k_B$  is the Boltzmann constant,  $\tau_0$  is a characteristic time, and  $T$  is the temperature. Superparamagnetic behavior can be observed, using an instrument with a characteristic measuring time ( $\tau_i$ ), at temperatures above the blocking temperature ( $T_{B1}$ ), which is defined by

$$T_{B1} = \frac{CV}{k_B [\ln(\tau_i/\tau_0)]}. \quad (2)$$

Superparamagnetism and the associated blocking phenomenon have been observed in magnetic granular materials by several techniques.<sup>5-9</sup> However, if only one measuring time is employed,  $\tau_0$  and  $CV$  cannot be independently determined. The situation is vastly improved if one can employ two measuring techniques with widely different characteristic times. The two techniques we employed were SQUID magnetometry and  $^{57}\text{Fe}$  Mössbauer spectroscopy with characteristic times of  $\tau_1 \approx 10$  s and  $\tau_2 \approx 10^{-8}$  s, respectively.<sup>7</sup> Furthermore, by extrapolation from the results of the low-field measurements, the characteristics at zero applied field, for which Eq. (1) is defined, can be extracted.

In magnetometry,  $T_{B1}$  can be located by noting the temperature at which remanence (see Fig. 2) and coercivity (see Eq. (6) below) reduce to zero. It can also be marked by the peak of the zero-field-cooled magnetization under a small field as shown in Fig. 3. In  $^{57}\text{Fe}$  Mössbauer spectroscopy, the value of  $T_{B2}$  can be determined by noting the temperature at which the magnetic hyperfine interaction first appears.

With two measuring times, one obtains from Eq. (2)

$$\frac{T_{B1}}{T_{B2}} = \frac{\ln(\tau_2/\tau_0)}{\ln(\tau_1/\tau_0)}, \quad (3)$$

which is independent of  $CV$ , hence sample. It may be noted that as long as  $\tau/\tau_0$  is a function of  $CV/k_B T$ , not necessarily an exponential function,  $T_{B1}/T_{B2}$  will be independent of the sample. Using Eqs. (2) and (3) one obtains separately

$$\tau_0 = \tau_1^{1/[1 - (T_{B2}/T_{B1})]} \tau_2^{1/[1 - (T_{B1}/T_{B2})]}, \quad (4)$$

$$CV = k_B T_{B1} [\ln(\tau_1/\tau_2) / (1 - T_{B1}/T_{B2})]. \quad (5)$$

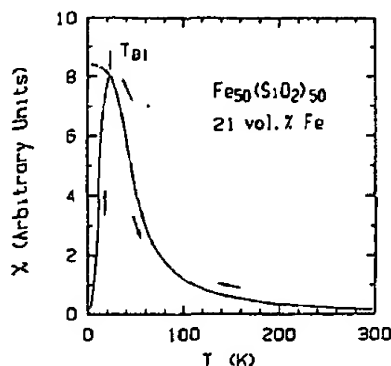


FIG. 3. Typical zero-field-cooled and field-cooled magnetic susceptibility vs temperature curve with an applied field of 50 Oe.

A large number of granular samples with low  $x$ , have been measured by both techniques.<sup>7</sup> As shown in Table I, indeed the same ratio  $T_{B1}/T_{B2} \approx 0.35$  has been obtained for all granular samples, indicating that  $\tau_0$  is independent of sample. Using  $\tau_1 \approx 10$  s,  $\tau_2 \approx 10^{-8}$  s, and  $T_{B1}/T_{B2} \approx 0.35$ , one obtains  $\tau_0 \approx 1.4 \times 10^{-13}$  s. Of course, if a stretched exponential relaxation time is assumed, the  $\tau_0$  value will be modified. The average diameters of the small particles obtained from TEM are 25 and 38 Å for  $\text{Fe}_{50}(\text{SiO}_2)_{50}$  and  $\text{Fe}_{60}(\text{SiO}_2)_{40}$ , respectively. Consequently the magnetic anisotropy constant  $C$  is about  $1 \times 10^7$  erg/cm<sup>3</sup>. This value is about two orders of magnitude larger than bulk magnetocrystalline anisotropy of Fe ( $K_1 = 1 \times 10^5$  erg/cm<sup>3</sup>). Similarly large differences in  $C$  and  $K_1$  have been found in other systems.<sup>10</sup> Thus it is apparent that the total anisotropy energy in granular magnetic solids is dominated by contributions (e.g., stress and surface) other than the magnetocrystalline anisotropy.

Below  $T_B$ , coercivities of single domain particles are generally much larger than that of bulk material. The temperature dependence of  $H_c$  is dominated by superparamagnetic relaxation which leads to<sup>11</sup>

$$H_c(T) = H_c(0) \left( 1 - \sqrt{\frac{T}{T_B}} \right). \quad (6)$$

This  $\sqrt{T}$  dependence has been observed in many granular Fe specimens.<sup>12,13</sup>

TABLE I. Deposition temperatures, blocking temperatures obtained from SQUID ( $T_{B1}$ ), Mössbauer ( $T_{B2}$ ), and the ratio ( $T_{B1}/T_{B2}$ ) for various granular samples.

Sample (at. %)	Deposition temperature (K)	SQUID $T_{B1}$ (K)	Mössbauer $T_{B2}$ (K)	Ratio $T_{B1}/T_{B2}$
$\text{Fe}_{50}(\text{SiO}_2)_{50}$	300	30	86	0.349
$\text{Fe}_{60}(\text{SiO}_2)_{40}$	300	58	167	0.347
$\text{Fe}_{60}(\text{SiO}_2)_{40}$	670	158	448	0.353
Co-sputtered Fe-(SiO <sub>2</sub> )	300	44	123	0.358

Above  $T_B$ , in the superparamagnetic state, the magnetization curve  $M(H)$  of a noninteracting system with uniform particle size is described by the Langevin function<sup>4</sup>:

$$M = pM_s L\left(\frac{\mu H}{k_B T}\right) = pM_s \left[ \coth\left(\frac{\mu H}{k_B T}\right) - \frac{k_B T}{\mu H} \right], \quad (7)$$

where  $p$  is the volume fraction of the magnetic particles,  $\mu = M_s V$  is the magnetic moment of a single particle with volume  $V$ , and  $H$  is the external field. Because  $\mu$  is large ( $\approx 10^2 - 10^3 \mu_B$ ), saturation of the magnetic moments cannot be accomplished particularly at  $T > T_B$ . In all real systems, there are size distributions. The resultant magnetization should be given by

$$M = pM_s \int_0^\infty L\left(\frac{M_s V H}{k_B T}\right) f(V) dV, \quad (8)$$

where  $L$  is the Langevin function as before and  $f(V)$  is size distribution. Assuming spherical particles of diameter  $D$  for simplicity, a log-normal size distribution,

$$f(D) = \frac{1}{\sqrt{2\pi} \ln \sigma} \exp \left[ -\frac{(\ln D - \ln \bar{D})^2}{2(\ln \sigma)^2} \right], \quad (9)$$

is most often used. Thus by fitting the experimental data  $M(H)$  to Eq. (8), one can obtain the distribution characterized by  $\bar{D}$  and  $\sigma$ . Our results<sup>14</sup> show that the sizes determined are in good agreement with those of TEM.

Other distinctive features of granular magnetic systems are the susceptibility ( $\chi$ ) and its temperature dependence. For conventional paramagnetic systems with atomic moments,  $\chi$  has the well-known Curie-Weiss form of

$$\chi = \frac{np_{\text{eff}}^2 \mu_B^2}{3k_B(T - \theta)}. \quad (10)$$

Consequently,  $1/\chi$  will be linear in  $T$ . In the case of granular magnetic systems at  $T > T_B$ , one obtains, using Eq. (7),

$$\chi = \frac{pV M_s^2(T)}{3k_B T} \quad \text{for } \mu H < k_B T, \quad (11)$$

for noninteracting granules. By including interactive effects, following Chantrell and Wohlfarth,<sup>15</sup>

$$\chi \propto \frac{M_s^2(T)}{T - T_0}. \quad (12)$$

Because of the temperature dependence of  $M_s(T)$ ,  $1/\chi$  is not linear in  $T$ . This is indeed observed experimentally. The  $T_0$  value can be located in the plot of  $1/\chi$  vs  $T$  at which  $1/\chi$  reduces to 0.

Having obtained  $T_0$  for the samples, one can now deduce  $M_s(T)$ , the temperature dependence of the spontaneous magnetization of the ultrafine ferromagnetic particles.<sup>14</sup> Experimentally,<sup>14</sup> it has been found that  $\sqrt{\chi(T - T_0)}$  has a  $T^{3/2}$  dependence, i.e.,  $M_s$  follows Bloch's law:  $M_s(T) = M_0(1 - BT^{3/2})$ . The fact that  $T^{3/2}$  dependence is observed indicates that there are spin-wave excitations despite the small size of the ferromagnetic particles. However, the spin-wave constant  $B$  of the granular Fe particles is very different from that of the bulk Fe. The



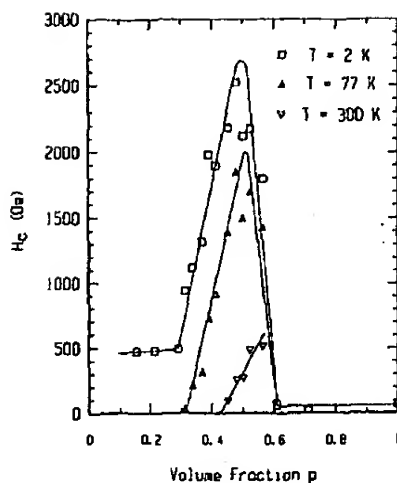


FIG. 4. Magnetic coercivities at 2, 77, and 300 K of granular Fe-SiO<sub>2</sub> films deposited onto room-temperature substrates as a function of Fe volume fraction.

spin-wave constants  $B$  obtained are  $4.30 \times 10^{-5} \text{ K}^{2/3}$  and  $4.46 \times 10^{-5}$  for Fe<sub>40</sub>(SiO<sub>2</sub>)<sub>60</sub> and Fe<sub>50</sub>(SiO<sub>2</sub>)<sub>50</sub>, respectively, considerably larger than the value of  $3.3 \times 10^{-6} \text{ K}^{2/3}$  for bulk Fe. There are several possibilities for the increase, among them, the abundance of the magnetic surfaces,<sup>16</sup> a modification of the spin-wave spectrum, and a cutoff of the spin waves with wavelength larger than the physical dimension of the particles.<sup>14</sup>

#### IV. ENHANCED FERROMAGNETIC PROPERTIES OF GRANULAR Fe SYSTEMS

Granular Fe-SiO<sub>2</sub> samples have been fabricated across the entire metal volume fraction range  $0 < x_v < 1$  to reveal the evolution of the magnetic properties. In Fig. 4 we show the coercivity ( $H_c$ ) at 2, 77, and 300 K for a set of samples of granular Fe-SiO<sub>2</sub> deposited on room temperature substrates. The  $H_c$  data at 2 K are close to the ground-state properties. Below the percolation threshold ( $x_v < x_p$ ), one observes a giant enhancement of  $H_c$ , reaching a peak of 2500 Oe. As  $x_v$  is increased further,  $H_c$  precipitously drops to a value of about  $H_c \approx 50$  Oe, which is close to the value of sputtered bulk Fe.  $H_c$  remains at that value from  $x_v = 60\%$  to  $100\%$ . For a given sample of  $x_v < x_p$ ,  $H_c$  decreases as  $\sqrt{T}$  which is consistent with Eq. (6).

For samples deposited at room temperature, larger particle sizes are realized in samples with higher values of  $x_v$ . Therefore, the observed increase of  $H_c$  may be associated with the increase of particle size. This indeed is supported by the following experiment.<sup>17</sup> We deposited samples with the same volume fraction (29%) but at different substrate temperature  $T_s$ , which effectively enlarges the particles. The value of  $H_c$  at 6 K varies from 500, 800, 1500, and 2200 Oe for samples deposited at  $T_s = 300, 475, 675$ , and 875 K respectively. Apparently,  $H_c(0)$  in Eq. (6) increases with particle size.

There are three anomalies in the behavior of  $H_c$  in the granular Fe-SiO<sub>2</sub> system. First, the experimental results

establish that  $H_c$  increases dramatically with particle size. Second, extremely high  $H_c$  values (at least 2500 Oe) are achieved. According to conventional theories,<sup>5,6</sup> for single domain particles, the zero-temperature coercivity is about  $2K_1/M$ , which is independent of size. But  $2K_1/M$  gives a coercivity of only 600 Oe. The chain-of-spheres fanning mode could provide a maximum  $H_c$  of 2700 Oe for an infinitely long chain in a random system. Particles with large aspect ratio could also give  $H_c$  up to 5000 Oe. These extreme particle shapes and morphology were not revealed in the TEM micrographs. Finally, the total anisotropy constant  $C$  is at least two orders of magnitude larger than  $K_1$ . An adequate explanation must account for all the anomalous results. For example, the importance of shape anisotropy has been inferred in FMR measurements.<sup>18</sup> But they cannot account for all the experimental results.

However, it must be recognized that almost all the existing models assume free-standing particles dispersed in a nonbonding medium. In the granular Fe-SiO<sub>2</sub> system, the particles are strongly bonded to the insulating matrix and may be subjected to very large stresses. The metal-insulator interfaces may dominate the coercivity in such systems. The large values of  $H_c$  may be related to the experimental fact that  $C \gg K_1$  as mentioned earlier.

If the high values of  $H_c$  and magnetization already realized can be further improved, granular Fe-SiO<sub>2</sub> offers much promise as a magnetic recording medium. For high density recording, the amplitude and width are roughly proportional to  $\sqrt{M H_c}$  and  $\sqrt{1/H_c}$ , respectively.<sup>19,20</sup> Larger  $H_c$  and  $M$ , thus assure better recording characteristics. The low temperature values of  $H_c$  and  $M$ , of granular Fe-SiO<sub>2</sub> have already exceeded those of common recording media. If the excellent properties can be preserved to room temperature, we would have an excellent recording media. Another important consideration is that of recording noise, which roughly scales with the particle size. Granular Fe-SiO<sub>2</sub>, containing ultrafine particles, enjoys great advantage in this regard.

The coercivity data shown in Fig. 4 are from samples deposited onto room-temperature substrates, where the metal granules are relatively small. Consequently,  $H_c$  at room temperature is much reduced by a combination of smaller  $H_c(0)$  and  $T_B$  as described in Eq. (6). Since both  $H_c(0)$  and  $T_B$  depend sensitively on the particle size even a modest increase of particle size (e.g., a factor of 2) would significantly alter the temperature dependence of the magnetic properties.

The composition Fe<sub>75</sub>(SiO<sub>2</sub>)<sub>25</sub> with  $x_v = 0.42$  was chosen for further exploration<sup>21</sup> because a maximum in  $H_c$  has been achieved near that volume fraction as shown in Fig. 4. A number of process conditions such as sputtering gas pressure, deposition rate, substrate temperature were varied in order to increase the granule size. Of those, the substrate temperature was found to be most effective. For samples deposited at  $77 \text{ K} < T_s < 400 \text{ K}$ , the granules are about 40 Å. Above  $T_s = 400 \text{ K}$ , granule sizes increase with increasing  $T_s$ . The samples deposited at  $T_s = 575 \text{ K}$  contain grains of about 60 Å, and  $T_s = 775 \text{ K}$  yields grains of about 150 Å. By increasing the granule size, as facilitated

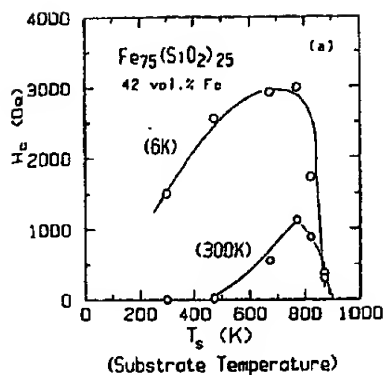


FIG. 5. Variation of coercivity  $\text{Fe}_{75}(\text{SiO}_2)_{25}$  ( $x_p = 0.42$ ) at 6 and 300 K as a function of substrate temperatures.

by higher  $T_p$ , the coercivity is dramatically affected in both magnitude and temperature dependence. As shown in Fig. 5,  $H_c$  at 6 K increases from 1.5 kOe to about 3 kOe as  $T_s$  is increased from 300 to 775 K. For samples with  $T_s > 800$  K,  $H_c$  at both 6 and 300 K decreases precipitously, due to sintering between the granules. The partially connected granules effectively allow the formation of multidomain structures, thus reducing  $H_c$ . A maximum of  $H_c$  at both 6 and 300 K is achieved with  $T_s = 775$  K. The values of  $H_c$  of 3 kOe (at 6 K) and 1.1 kOe (at 300 K) are among the highest for Fe particles. The high value at 300 K together with a large magnetization of 160 emu/g are particularly encouraging for possible recording media applications. Recently, these large values of  $H_c$  have been confirmed by others.<sup>22</sup>

Finally, it should be mentioned that the superior magnetic properties of the granular solids are microstructure controlled and can be tailored through process conditions. The insulating matrix (e.g.,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) greatly enhances the chemical stability of the magnetic particles, and the wear and corrosion resistance of the media. Furthermore, since vapor deposition is the most effective method of making granular metal films, the fabrication, dispersion, and protection of the ultrafine granules, as well as coating onto desired surfaces suitable for device applications, are achieved in a single process.

## V. GRANULAR ALLOY SYSTEMS

Almost all studies of granular materials performed to date have been restricted to systems involving a single elemental metal. Ultrafine metal alloys, both crystalline and amorphous, remains largely unexplored despite the fact that alloys have almost always proven to be more useful and interesting than their pure metallic constituents. We have recently succeeded in the fabrication of granular alloys of Fe-Ni, Fe-Co, Fe-B, and Fe-Cu in a variety of matrices.<sup>10</sup> Of these, Fe-Cu is an example of a metastable crystalline alloy and Fe-B is amorphous.

The coercivity of the  $(\text{Fe}_{50}\text{Ni}_{50})_x(\text{Al}_2\text{O}_3)_{1-x}$  alloy system is shown in Fig. 6. The value of the coercivity changes smoothly as the metal content is increased, and

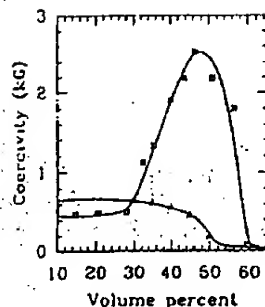


FIG. 6. Coercivity vs volume fraction for granular Fe-SiO<sub>2</sub> (squares) and granular  $(\text{Fe}_{50}\text{Ni}_{50})\text{-Al}_2\text{O}_3$  (triangles).

drops off sharply at the percolation threshold.<sup>10</sup> This is precisely the expected behavior of  $H_c$  in granular magnetic system when the percolation threshold is crossed. It also underscores the anomalous features of  $H_c$  in granular Fe-SiO<sub>2</sub> which are shown in Fig. 6 for comparison. It should be mentioned that very similar behavior is also observed in the  $(\text{Fe}_{50}\text{Ni}_{50})_x(\text{SiO}_2)_{1-x}$  system.

The case of granular metastable crystalline Fe-Cu alloys is more challenging. Under equilibrium conditions, Fe and Cu are immiscible with one another. We have earlier demonstrated that, by vapor quenching, metastable  $\text{Fe}_x\text{Cu}_{1-x}$  can be formed at any composition.<sup>23</sup> We will mention granular samples of the metastable alloy  $\text{Fe}_{35}\text{Cu}_{65}$  with  $T_c = 250$  K. Samples of  $(\text{Fe}_{35}\text{Cu}_{65}) - (\text{Al}_2\text{O}_3)$  with  $x_p = 40\%$  have been deposited at various substrate temperatures. If the substrate are maintained at 100 °C or below, granular fcc  $\text{Fe}_{35}\text{Cu}_{65}$  can be achieved, with a blocking temperature of  $T_B = 80$  K. Below  $T_B$  coercivity is observed, with a value of  $H_c = 620$  G at 4.2 K. However, at higher substrate temperatures the metal segregate forming isolated grains of fcc Cu and bcc Fe.

Ultrafine Fe particles in an metallic matrix cannot be readily formed because Fe forms alloys or compounds with almost any metal. However, there are actually a few metallic elements with which Fe is immiscible. Copper is one such example as mentioned above. Because of the metastable nature of such Fe-Cu alloys, recrystallization will occur at elevated temperatures, with a transformation into separated phases of bcc Fe and fcc Cu. In the process, Fe forms small particles whose sizes can be controlled by the annealing conditions. In this manner the magnetic properties of these materials can be optimized.<sup>3</sup>

Typical behavior for the evolution of the magnetic properties at room temperature is shown in Fig. 7 for the case of  $\text{Fe}_{45}\text{Cu}_{55}$ , as it goes through an annealing sequence of 10 min at each annealing temperature ( $T_A$ ). The as-prepared metastable fcc  $\text{Fe}_{45}\text{Cu}_{55}$  alloy is a soft ferromagnet ( $T_C = 360$  K), with a very small  $H_C (< 10$  Oe) and a squareness ratio ( $\text{SQ} = M_r/M_s$ ) of less than 5% at room temperature. Up to  $T_A = 250$  °C, the magnetic properties do not change appreciably. However, the value of  $H_C$  increases dramatically between  $T_A = 250$  °C and  $T_A = 300$  °C, reaches a maximum of 526 Oe for  $T_A = 350$  °C and then decreases as  $T_A$  is increased further. The value of SQ behaves similarly, reaching a maximum of 40%, also at 350 °C.

X-ray diffraction and TEM show that the fcc structure

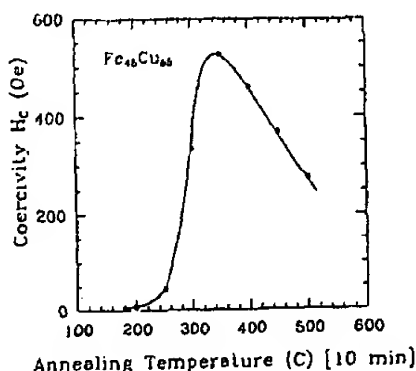


FIG. 7. Room temperature coercivity of  $\text{Fe}_{45}\text{Cu}_{55}$  after annealing at  $T_A$  for 10 min.

is preserved up to  $T_A = 250^\circ\text{C}$ . Following annealing at  $300^\circ\text{C}$ , however, the bcc  $\alpha$ -Fe lines suddenly appear, signaling the recrystallization of the metastable alloy into fcc Cu and bcc Fe. Thus the dramatic increase in  $H_C$  at  $T_A = 300^\circ\text{C}$  is the direct result of the appearance of small Fe particles. As  $T_A$  is increased past  $300^\circ\text{C}$ , the particle size increases from 15 nm at  $T_A = 300^\circ\text{C}$  to 60 nm at  $T_A = 500^\circ\text{C}$ . Eventually, when the critical size is exceeded or Fe grains come into contact, the enhanced magnetic properties begin to deteriorate.

More recently, we have begun a study of granular spin glass systems. This is motivated by the fact that the critical dimension<sup>24</sup> for spin glass ordering is believed to be between 2 and 3. Spin glass ordering is observed in 3D systems, but as one reduces the spin glass film thickness, the spin glass transition ( $T_g$ ) shifts to low temperatures due to finite size effects.<sup>25,26</sup> For sufficiently thin samples, where the correlation length exceeds the film thickness, 2D behavior has been observed.<sup>26</sup> We used multilayer of  $\text{CuMn}/\text{Al}_2\text{O}_3$  in a layer geometry. For a spin glass layer of  $\text{Cu}_{92}\text{Mn}_8$  with a thickness  $W$ ,  $T_g(W)$  can be excellently described by a simple finite-size scaling relation

$$\frac{T_g(\infty) - T_g(W)}{T_g(\infty)} = \epsilon = A W^{-\lambda} = \left(\frac{W}{W_0}\right)^{-\lambda}, \quad (13)$$

with  $T_g(\infty) = 34\text{ K}$ ,  $\lambda = 0.64 \pm 0.07$ ,  $A = 6.7 \pm 0.25$ , and  $W_0 = 19.5 \pm 1.1\text{ \AA}$ . For  $W < W_0$ ,  $T_g(W)$  would be zero.

In the spin glass granular system of  $\text{Cu}_{92}\text{Mn}_8$  in an  $\text{Al}_2\text{O}_3$  matrix, no spin glass transition can be observed for particle size of about 15  $\text{\AA}$ , consistent with finite size effects observed in layered spin glasses. For samples above the percolation threshold, spin glass ordering exists but with a depressed  $T_g$  according to the metal volume fraction. These very interesting preliminary results indicate a new realm for the exploration of granular magnetic systems.

## VI. SUMMARY

Granular magnetic solids are a good example of artificially structured materials. Starting from two very ordinary materials, Fe and  $\text{SiO}_2$  for example, granular  $\text{Fe-SiO}_2$

may be produced and seen to display a rich variety of physical properties. Below the percolation threshold the magnetic properties of an assembly of isolated single-domain particles of nanometer sizes have been studied in considerable detail. Across the percolation threshold, enhanced magnetic properties, particularly coercivity, have been uncovered. The improved properties show potential for applications, among them, as magnetic recording media. Further exploration of granular magnetic solids of other magnetic elements and alloys are in progress.

## ACKNOWLEDGMENT

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